

# Characterization of Different Types of Diesel (EGR Cooler) Soot Samples

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## ABSTRACT

Soot fouling on exhaust gas recirculation coolers (EGRC) decreases thermal efficiency, implying the unfulfillment of  $\text{NO}_x$  standards, and increases the pressure drop producing the malfunctioning of this device. The characterization of soot is of great interest since soot physico-chemical properties may have a direct influence on the degree of malfunctioning of EGRC. Thus, the combined analysis and interpretation of all the soot physico-chemical features are essential to correctly interpret its behavior when soot is deposited on the EGRC walls. In this context, the aim of this study is the characterization of five different types of diesel soot which were collected from several high pressure EGRC, working at different conditions (engine bench and vehicle). Each soot sample was characterized by means of elemental analysis, specific surface area (BET method), FESEM, FTIR, TGA, GC-MS and UV-visible spectroscopy. Besides, some of the carbon samples were also characterized by TEM, XRD and Raman spectroscopy. From the results obtained from all these techniques it can be concluded that there exist marked physical and chemical differences between bench and vehicle soot samples. Vehicle soot samples presented an important quantity of functional groups, both aliphatic species (coming from lube oil and/or unburned fuel) and some oxygenated compounds, probably adsorbed on soot surface. Moreover, regarding internal structure of primary particles, bench soot shown two major parts: an inner core and an outer shell, while vehicle soot exhibited very disordered structure (almost turbostratic, i.e., amorphous).

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## INTRODUCTION

A substantial percentage of trucks, buses, cars, ships, etc., are powered by diesel engines which produce many tons of air pollutants. Therefore, reducing diesel pollution has become a public priority. Some of the main pollutants of the exhaust gases from these engines are particulate matter (like soot) and nitrogen oxides ( $\text{NO}_x$ ) [1,2,3,4].

The way the combustion is produced as well as the fuel characteristics, among others, strongly influence the growth of soot particles [5]. Soot is produced during the incomplete combustion and is composed of fine particles of carbon coated with organic chemicals. For instance, with polycyclic aromatic hydrocarbons, or PAH, which are well-known to be harmful to human health [6,7], and besides they are considered to contribute to soot inception process [8,9]. Moreover, soot formation in diesel engines, and therefore the possible soot deposition on different devices, can also have a negative influence on these vehicles. It is well-known, soot deposition on exhaust gas recirculation cooler, EGRC, produces the malfunctioning of this device [10], and this fact may lead to the unfulfillment of  $\text{NO}_x$

standards. The increase of soot fouling implies a decrease of thermal efficiency and the raise of pressure drop what involves greater EGR gas temperature and lower EGR gas flow.

In this context, the aim of this work is to characterize 5 different types of diesel soot (DS) samples, collected from high pressure (HP) EGRC, in order to give not only a general overview of soot characterization but to delve into real diesel soot physico-chemical properties coming from different running tests. DS samples were analyzed in terms of C, H and N assessment (elemental analysis), surface area (BET method), morphology by field emission scanning electron microscopy (FESEM), surface functionalization (infrared spectroscopy, FTIR) and structure and thermal resistance (thermogravimetric analysis, TGA). Gas chromatography coupled with mass spectrometer (GC-MS) was also used for the evaluation of light species, including PAH, adsorbed on soot surface and removed by dichloromethane (DCM) washings. Besides, two DS were analyzed by transmission electron microscopy (TEM), X-ray

diffraction (XRD) and Raman spectroscopy. These characterization techniques have been chosen due to their demonstrated suitability for carbonaceous materials [11].

## SOOT SAMPLES AND EXPERIMENTAL INSTALLATIONS

In this section, the materials employed as well as the experimental installations used are described.

### Carbon Materials

Five diesel soot samples were characterized. Two of these samples, named DS6 and DS9, were collected from a diesel engine bench, while the other three, named DS14, DS17 and DS19 (Figure 1), were recovered from a vehicle after covering a given number of kilometers. The formation conditions of these DS are shown in Table 1.



Figure 1. Pictures of DS14, DS17 and DS19 on the HP EGRc devices.

Table 1. Matrix with the general conditions of the formation of DS samples: engine bench and vehicle.

|      | HC (ppm) | T gas (°C) | Duration (h) | Mileage (km) | Time (months) |
|------|----------|------------|--------------|--------------|---------------|
| DS6  | 200      | 450        | 8            | --           | --            |
| DS9  | 500      | 500        | 8            | --           | --            |
| DS14 | --       | --         | --           | 24663        | 13            |
| DS17 | --       | --         | --           | 46707        | 12            |
| DS19 | --       | --         | --           | 110238       | 24            |

On the one hand, the two engine bench soot samples were collected from the same engine bench: Renault M9R 2.0L 150 CV, but with different EGRc by using several operation conditions (Table 1). On the other hand, the three vehicles soot samples were collected from different vehicles of the same brand. The three vehicles went through a public road and traffic in town test. In addition, these vehicles are in the same medium-sized light commercial vehicle and people mover range. Specifically, in the US market segment these vehicles are classified as *minivans* and as *m-segment multipurpose cars* in the Euro market segment.

In order to analyze the adsorbed species on soot surface by means of GC-MS and UV-visible spectroscopy, solvent extraction was performed. With this purpose, 20 mg of soot were suspended in 10 mL of DCM by using an ultrasonic bath for 30 minutes. After this time, the suspension was filtrated under vacuum on a Teflon filter (Millipore 0.50  $\mu\text{m}$ ) (Figure 2). The species soluble in DCM, named soluble organic fraction (SOF), remained in the solvent (the extract presents a yellow-brown color, Figure 2), while the insoluble carbonaceous material trapped on the filter (washed soot). From now onward, the samples called “washed soot” will imply that they have been treated following this procedure. The samples may also be called with the prefix “W” before the acronym of the solid (like WDS6, WDS9, etc.).

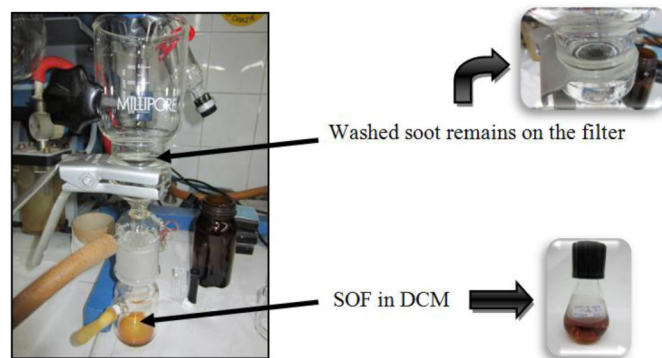


Figure 2. Filtration device to obtain the washed soot on the filter and the SOF (DCM solution) [12].

The washed soot and the raw soot samples were also analyzed by UV-visible spectroscopy. To this aim a weighed quantity of washed and/or raw soot was suspended in N-methyl-pyrrolidinone (NMP), by using an ultrasonic bath for about 30 min.

### Experimental Installations

FTIR, BET method, elemental analysis, TGA and GC-MS techniques were conducted in the *Istituto di Ricerche sulla Combustione-C.N.R.*, Naples (Italy). The Technical Services from the University of Alicante (Spain) performed the TEM, XRD and Raman spectroscopy analyses, and Technical Services from the University of Zaragoza (Spain) carried out the FESEM analysis.

Following, the description of the installations and equipments used in the *Istituto di Ricerche sulla Combustione (I.R.C.) -C.N.R.* are described:

- Elemental analysis: carbon, hydrogen and nitrogen content (by weight) were measured by a Perkin-Elmer 2400 CHNSO elemental analyzer. The oxygen amount was evaluated by difference.
- BET method: BET specific surface area of the samples was measured by  $\text{N}_2$  adsorption at  $-196^\circ\text{C}$  using a Quantachrome Autosorb 1-C. Each sample was outgassed under vacuum at  $110^\circ\text{C}$  before the analysis. Data were processed according to BJH method.
- FTIR: Fourier transform infrared spectra were recorded on a Nicolet iS10 spectrometer, using the attenuated total reflectance (ATR) method by using a germanium crystal. The spectra were acquired in the  $600\text{--}4000\text{ cm}^{-1}$  range on the powdered samples without KBr addition.
- TGA: thermogravimetric analyses were performed on a Perkin-Elmer Pyris 1 thermogravimetric analyzer. The samples were heated both in oxidant (air) and in inert (nitrogen) environment ( $30\text{ mL/min}$ ) from  $30^\circ\text{C}$  up to  $900^\circ\text{C}$  at a rate of  $10^\circ\text{C/min}$ .
- GC-MS: SOF obtained from each raw sample was analyzed on a HP6890 gas chromatograph, coupled with a HP5975A mass spectrometer. The GC was equipped with an Agilent HP-5MS capillary column ( $30\text{ m} \times 0.25\text{ mm i.d.}$ ,  $0.25\text{-}\mu\text{m}$  film thickness). Helium has been used as carrier gas with a constant flow of  $1.0\text{ mL/min}$ . The oven temperature was programmed at  $40^\circ\text{C}$  and held for 3 min, then it was raised to  $300^\circ\text{C}$  at a heating rate of  $5^\circ\text{C/min}$ .

°C/min and held at 300 °C for 20 min. A sample volume of 1 µL was injected. The MS was operated in electron ionization mode, and a range from 50 to 600 m/z was scanned.

- UV-visible spectroscopy: UV-visible spectra of SOF in DCM and of soot (raw or washed soot) suspended in NMP, were obtained on a HP 8453 Diode Array spectrophotometer by using 1 cm path-length quartz cuvette. The interference of the solvent (NMP) on the UV absorption limits the visualisation of the spectra to 260-1000 nm region.

## RESULTS AND DISCUSSION

In this section, main results obtained from the different techniques are presented and discussed.

### Elemental Analysis

Elemental analysis mainly allows the quantification of carbon, hydrogen and nitrogen. Also, in the case of carbonaceous materials, it is used to evaluate the molar H/C ratio values, for instance, to evaluate the amount of active C-H sites available for oxidative attack [13]. Table 2 presents the % wt. values obtained for the different soot samples for C, H and N. Oxygen values were also reported by difference.

Elemental analysis indicates that in all raw DS samples the amount of C is around 70-83 % wt. Vehicle soot presented larger H content (3-5 % wt.) than engine bench soot (0.4-1 % wt.). The H/C molar ratio of vehicle soot exhibited high values (0.61-0.88) compared to engine bench soot (0.06-0.18).

In general, on the one hand, a high H/C ratio value is related both to a high SOF content and to a high number of available active sites on soot surface which imply a high reactivity of the material toward oxygen [14]. On the other hand, a low H/C molar ratio (lower than 0.1), like DS9 sample, is indicative of a high graphitic nature as observed in other carbon-based materials, such as combustion-derived soot with a high degree of maturation in the combustion system [13,15,16], and it is in contrast to the other diesel soot samples with even larger H/C ratio values from 0.1 to 0.8, Table 2. Therefore, these high values reflect the presence of an elevated quantity of functional or molecular groups.

Additionally, this analysis was also performed on washed samples. In Table 2, it may be observed that H/C ratio values decreased when samples were washed with DCM. This fact suggests a significant presence of SOF species adsorbed on the surface of raw soot, mainly aliphatic hydrocarbons coming from lube oil and/or unburned fuel.

Regarding the oxygen content, it may be observed that this concentration is quite elevated compared to other diesel soot surrogates [4,14]. The presence of oxygen functional groups is of interest in terms of soot reactivity, thus, in order to be able to eliminate the soot by oxidation.

Table 2. Elemental analysis and H/C molar ratio of the different soot samples.

|       | Elemental analysis<br>(% wt.) |      |      | H/C ratio<br>(molar) | O*<br>(% wt.) |
|-------|-------------------------------|------|------|----------------------|---------------|
|       | C                             | H    | N    |                      |               |
| DS6   | 83.08                         | 1.26 | 0.85 | 0.181                | 14.81         |
| WDS6  | 86.81                         | 0.70 | 1.22 | 0.097                | 11.27         |
| DS9   | 80.75                         | 0.40 | 0.43 | 0.059                | 18.42         |
| WDS9  | 79.24                         | 0.32 | 1.08 | 0.048                | 19.36         |
| DS14  | 74.44                         | 5.48 | 2.09 | 0.883                | 17.99         |
| WDS14 | --                            | 4.35 | 2.78 | 0.530                | --            |
| DS17  | 69.43                         | 3.51 | 1.55 | 0.606                | 25.51         |
| WDS17 | 72.03                         | 1.93 | 1.78 | 0.322                | 24.26         |
| DS19  | 71.52                         | 3.78 | 0.64 | 0.633                | 24.06         |
| WDS19 | 72.62                         | 2.32 | 2.16 | 0.383                | 22.90         |

\*By difference

### Specific Surface Area (BET Method)

Specific surface area values of raw soot samples, Table 3, were determined by using the Brunauer-Emmett-Teller (BET) method [17]. It can be observed that vehicle soot samples (DS14, DS17 and DS19) presented very low values, while the bench soot samples (DS6 and DS9) showed relatively high values.

Table 3. Specific surface area values with BET method ( $S_{BET}$ ) for the different soot samples.

|      | $S_{BET}$ (m <sup>2</sup> /g) |
|------|-------------------------------|
| DS6  | 119                           |
| DS9  | 93                            |
| DS14 | < 1                           |
| DS17 | 17                            |
| DS19 | 4                             |

One explanation for this difference is that vehicle samples present a larger quantity of adsorbed compounds (the SOF) than bench soot samples on soot surface, which clog the entrance to the pores of soot [12]. In order to check this possibility, sample DS9 and DS19 were treated at 1000 °C in an inert atmosphere of nitrogen (called DS9-1000 and DS19-1000). From the analyses of these treated samples were obtained a specific surface area equal to 451 and 490 m<sup>2</sup>/g, respectively. This result confirms the existence of a great amount of adsorbed compounds on both types of samples (probably aliphatic hydrocarbons, coming from lube oil and/or unburned fuel, and/or oxygenated compounds which were already suggested by the elemental analysis).

However, with the thermal treatment, the pore structure may change because of the high temperature. Therefore, another BET analysis was carried out with WDS6 sample (WDS6 is the result of washing DS6 sample with DCM to remove the SOF). From this analysis, WDS6 resulted to reach a specific surface area equal to 155 m<sup>2</sup>/g, corroborating that these adsorbed compounds clog the soot pores since they block the entrance to N<sub>2</sub> molecules.

Moreover, the t-method [18] was also employed in order to study the possible developing of microporosity during the thermal treating and, therefore, the misunderstanding in BET specific surface area measurement. The t-equation (according to ASTM standard D-6556-01) was applied to the following samples: DS6, WDS6, DS9, DS9-1000, DS14, DS17 and DS19. A significant microporosity was acquired by DS9-1000 sample, reaching a value of 241 m<sup>2</sup>/g of the total 451 m<sup>2</sup>/g. On the other hand, no microporosity was obtained

neither for raw samples nor for WDS6. This result was expected for original soot samples (since the adsorbed compounds could be blocking the pores). However, the negligible microporosity of WDS6 suggests that the thermal treatment generates the developing of microporosity in the carbon soot samples (changing the pore structure) besides the removal of adsorbed compounds [12].

### Electron Microscopy

The electron microscopy allows obtaining information about microstructure and nanostructure of the samples. Microscopy techniques can be used to analyze the structural and morphological properties of soot, such as shape, size, distribution of the particles, and graphene layer orientation [19]. From a general point of view, field emission scanning electron microscopy (FESEM) provides images of the surface morphology, whereas transmission electron microscopy (TEM) looks into the internal structure of solids and analyzes the microstructural details [19,20].

### Field Emission Scanning Electron Microscopy

In Figure 3, FESEM images reveal mostly spherical morphology of DS6 and DS9 soot particles (Figures 3a and 3b, respectively), joined together to create particle aggregates of variable sizes. However, DS17, DS14 and DS19 soot particles did not present such a clear spherical shape (Figures 3c, 3d, 3e), rather irregular

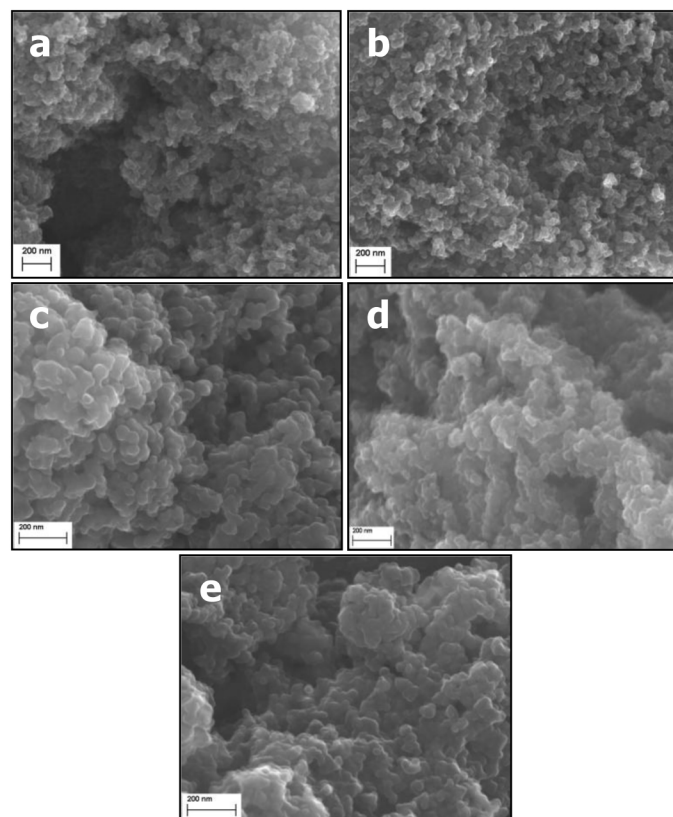


Figure 3. FESEM images: a) DS6, b) DS9, c) DS14, d) DS17 and e) DS19.

### Transmission Electron Microscopy

TEM was applied to DS9 and DS17, as representative samples of bench engine and vehicle soot, respectively.

TEM micrographs of DS9 (Figures 4a and 4b) reveal the typical structure of inner core and outer shell for diesel soot [3,21,22], Figure 4a. Besides, it may be observed the typical chain like structure of primary particles [3,4,23], Figure 4b.

Nevertheless, DS17 images (Figures 4c and 4d) present single and shorter graphene layers with no particular orientation relative to one another, i.e., turbostratic. This amorphous feature is more typical from chars [24,25], where randomly-oriented graphene layers may be observed. According to Hays and Vander Wal [26], hydrocarbons, oxygenated compounds and/or hydrogen atoms are usual groups placed at the edge of the layers contributing to the disorganization of soot nanostructure. Hays and Vander Wal findings [26] are in agreement with DS17-TEM images and elemental analysis (Table 2), since the high value of H/C ratio and oxygen amount obtained for washed vehicle soot samples (i.e., not related to the compounds adsorbed on soot surface but to the compounds that take part of the soot matrix) may imply their higher disorder (by extrapolating DS17-TEM images results to all vehicle soot samples).

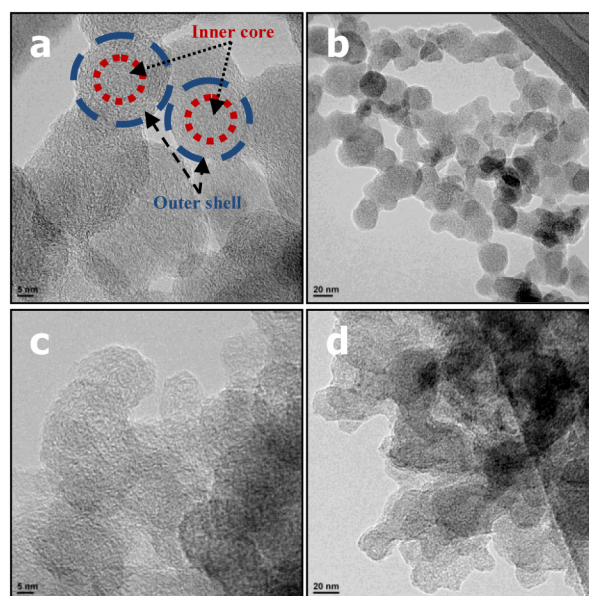


Figure 4. TEM images: a), b) DS9, c), d) DS17 soot samples.

By means of these two techniques, FESEM and TEM, it was possible to measure the mean diameter of the primary particles, Table 4. It may be observed that these values are quite similar and vary from 24 to 33 nm, and which are in the range of other diesel soot samples reported in literature [3,12, 21, 26,27,28]. It must be noticed that the size of the vehicle samples was obtained from irregular shaped particles.

Table 4. Mean values of the primary particle diameter (nm).

|      | Mean diameter (nm) |     |
|------|--------------------|-----|
|      | FESEM              | TEM |
| DS6  | 26                 | --  |
| DS9  | 27                 | 24  |
| DS14 | 31                 | --  |
| DS17 | 24                 | 25  |
| DS19 | 33                 | --  |